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Photostimulated vectorial electron transfer across the bilayer membrane of lipid vesicles in a system with CdS nanoparticles as photosensitizer and 1,4-bis(1,2,6-triphenyl-4-pyridyl)benzene as a reversible two-electron carrier

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Abstract

Photostimulated vectorial electron transfer through the lecithin bilayer membrane was studied in a system based on lipid vesicles with CdS as a photosensitizer located either in the vesicle inner cavity or outside the vesicles. 1,4-Bis(1,2,6-triphenyl-4-pyridyl)benzene (benzoviologen) was used as an effective lipophilic highly reversible electron carrier incorporated into the bilayer membrane. A peculiarity of this electron carrier is its ability to be reversibly reduced on one and two electrons. The interface electron transfer across the border "vesicular cavity–membrane" was studied by stationary and pulse photolysis. The primary photoreduced form of benzoviologen appears to be that reduced by one electron; however, on stationary photolysis, most benzoviologen molecules appear to be affected by two-electron reduction, which can result from the low mutual mobility of CdS nanoparticles and benzoviologen molecules. The CdS photostimulated transmembrane electron transfer from the internal sacrificial donor to the external acceptor (as regards the vesicular cavity) was performed for $[CoEDTA]^-$ as the final electron acceptor. The rate constants of electron transfer from the membrane-embedded two-electron reduced form of benzoviologen have been determined in the case of $[CoEDTA]^-$ and O_2 as acceptors.

Keywords: Electron transfer; Bilayer membrane; Photosensitizer

1. Introduction

Recently, many papers concerning photostimulated transmembrane electron transfer, assisted by cadmium sulfide semiconductor nanoparticles, incorporated into the inner cavities of surfactant vesicles have appeared (see for example [1,2]). Such photocatalytic systems, combining the advantages of a semiconductor as an efficient inorganic photosensitizer with the advantage of structural organization of the system, seem to be very promising for modeling the function of natural photosynthesis. Most typically, lipophilic viologens (derivatives of 4,4′-dipyridinium) are used as efficient primary electron acceptors or electron carriers in photocatalytic systems on the basis of lipid membranes. These compounds are characterized by high reversibility of the reactions of their one- and two-electron reduction and relatively negative values of reduction potentials. The most typical representative of these compounds is *N,N′*-dihexadecyl-4,4′-dipyridinium (cetylviologen) dication [2]. However, together with the above-mentioned advantages of cetylviologen as the transmembrane electron relay, it possesses also some serious shortcomings: (i) recently it was found difficult to modify the membrane with some anionic surface-active compound because formation of insoluble compound of cetylviologen occurs with such surfactants [3]; (ii) the value of the reduction potential of the reduced form of lipophilic viologens is not sufficient to carry out the electrochemical reaction of water reduction [4].

A more complicated compound 1,4-bis(1,2,6-triphenyl-4-pyridyl)benzene ("benzoviologen") was shown to have an advantage over the widely used lipophilic viologens when being employed as a transmembrane electron relay since its reduced forms possess more negative values of reduction potentials. Benzoviologen also possesses the chain of conjugated double bonds and therefore is probably able to serve as molecular "wire" providing electron transfer without motion of the molecule as a whole.

In the present paper we have carried out preliminary semiquantitative investigations aimed at clarification of benzo-

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viologen specificity as the electron relay in the systems on the basis of lipid vesicles sensitized by CdS nanoparticles.

2. Experimental details

2.1. Materials

The potassium salt (K_2[CdEDTA]) of cadmium ethylendiaminetetraacetate and the sodium salt (Na[CoEDTA]) of cobalt ethylendiaminetetraacetate were previously synthesized in the Laboratory for Catalytic Methods of Solar Energy Conversion of the Boreskov Institute of Catalysis, as described in [2]. Sodium sulfide (Na_2S) as well as sodium ethylendiaminetetraacetate (Na_2H_2EDTA) were of "pure" grade from Reakhim. Na_2S was used without further purification. The compounds for preparation of borate buffer with pH 8.2 were of "chemical pure" and "pure for analysis" grade. Distilled water was used for preparation of all water solutions. Acetonitrile was of "chemical pure" grade and used without further purification.

Colloidal solution of CdS particles with $2r \approx 50$ Å stabilized by polyacrylamide for adding to the outer water phase in the systems mentioned in Fig. 3(c) was prepared according to the procedure reported in [5].

The lipid vesicles were prepared using DL-β,γ-dimyristoyl-α-lecithin (DML) (Fluka AG), and DL-α-lecithin (Dipalmitoyl (DPL)) (Serva).

1,4-bis(1,2,6-triphenyl-4-pyridyl)benzene diperchlorate (benzoviologen ($bV(ClO_4)_2$)) was provided by NPO Monocrystall, Kharkov (now Ukraine). The structural formulae of the above compounds are shown in Fig. 1.

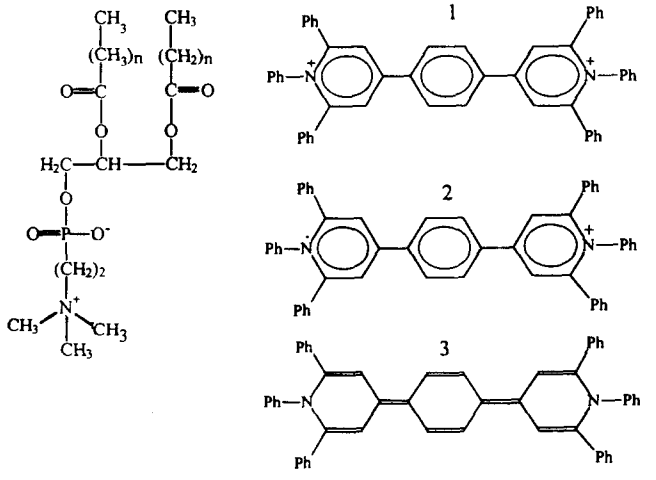

Fig. 1. Structural formula of lipids used for preparation of (a) lipid vesicles and (b) of benzoviologen and its reduced forms. For lipids, $n = 19$ for DPL, and $n = 17$ for DML. For viologens we have the following: 1, benzoviologen; 2, one-electron reduced form of benzoviologen ("red"); 3, two-electron reduced form of benzoviologen ("blue").

2.2. Methods

2.2.1. Preparation of vesicles

Approximately 20 mg of lecithin or dried mixture of lecithin with benzoviologen was dispersed in 1 ml of 0.3 M water solution of K_2[CdEDTA]. Benzoviologen was used in the form of acetonitrile solution. The procedure of vesicle synthesis was as in [3]. The resulting mixture was processed with ultrasound (22 kHz) for 20 min, centrifuged for 10 min and then passed through a gel filtration column filled with Sephadex G-50 medium. The vesicles containing fraction was separated according to the results of preliminary calibration with the use of colored vesicles. 0.45 M water solution of potassium chloride was used as an eluent.

The UV–visible optical absorption spectra were recorded in single and cyclic regimes and then processed by a Specord M400 spectrophotometer (Karl Zeiss Jena, Germany). A two-channel thermoregulated cellholder was used for the maintenance of constant temperature during the CdS particles growth.

2.2.2. Stationary photolysis

All experiments were carried out in anaerobic conditions. Dissolved oxygen was removed from the samples by passing Ar over their surface for 1–1.5 h while stirring the sample with a magnetic stirrer. This time appeared to be sufficient to remove most of the dissolved oxygen, because almost no induction period was observed on the curves of the benzoviologen reduced forms accumulation upon irradiation the samples with continuous laser source ($\lambda = 458$ nm). The samples were irradiated in standard hermetic 1 cm quartz cells.

A continuous argon laser ILA-120 (Karl Zeiss Jena) was used as a source of illumination with $\lambda = 458$ nm. The irradiation of the samples was carried out in the cell compartment of a Specol-20 spectrocolorimeter (Karl Zeiss Jena). The change in optical density, caused by the accumulation of one-electron ("red") ($bV^{\cdot+}$) and two-electron ("blue") (bV) reduced forms of benzoviologen in the membrane, was monitored at wavelengths of characteristic absorption maxima $\lambda = 525$ nm and $\lambda = 604$ nm respectively ($\epsilon_{525}{}^{b} = 8000\ M^{-1}\ cm^{-1}$, $\epsilon_{604}{}^{b} = 24\,000\ M^{-1}\ cm^{-1}$ and $\epsilon_{525}{}^{r} = 12\,500\ M^{-1}\ cm^{-1}$ [6]). For the initial form of benzoviologen the characteristic absorption maximum lies at 234 nm.

The intensity of the irradiation light was measured with an LM2 bolometer (Karl Zeiss Jena). During the irradiation, the samples were stirred with a magnetic stirrer; all measurements were carried out at temperature of 20 °C.

The quantum yields ϕ^{r} and ϕ^{b} of "red" and "blue" form accumulation in the membrane (per one electron) were calculated according to the following scheme:

$$\phi^{b} = 2\frac{W_0{}^{b}}{I_{abs}} = 2\frac{\Delta D_{604}}{I_{abs}\,\Delta t}\frac{VN_A}{\epsilon_{525}{}^{r} l}$$

$$\phi^r = \frac{W_0^r}{I_{abs}} = \frac{\Delta D_{525}^r}{I_{abs}\,\Delta t}\,\frac{VN_A}{\epsilon_{525}^r l}$$

$$\Delta D_{525}^r = \Delta D_{525} - \frac{\epsilon_{525}^b}{\epsilon_{604}^b}\,\Delta D_{604}$$

$$I_{abs} = I_0(1 - 10^{-D_{CdS}^{458}})$$

where W_0^b and W_0^r are the initial rates of "blue" and "red" form accumulation in the membrane in molecules per second, ΔD_{604} and ΔD_{525} are the changes in optical density of the sample at $\lambda = 604$ nm and $\lambda = 525$ nm respectively after a short period of time Δt, ΔD_{525}^r is the change in optical density caused by the absorption of the red form, the ϵ values are the extinction coefficients (see above), D_{CdS}^{458} is the optical density of CdS at $\lambda = 458$ nm, N_A is the Avogadro number, V is the volume of the sample, l is the cell length, and I_0 and I_{abs} are the intensities of the incident and absorbed light.

2.2.3. Pulse photolysis

In this method, home-built equipment was used [2]; the discharge energy of the pulse lamp was 200 J, the flash time being approximately 15 μs. The samples were irradiated with a light flash through a UFS-1 glass cut-off filter (transmissions at 240–500 nm and 640–2700 nm). A DKSSh-120 120 W xenon lamp, equipped with a ZhS-16 glass filter (transmission at 420–2700 nm) for cutting out the photoactive light was used as the source of the monitoring light. An SPM-2 monochromator (Karl Zeiss Jena) was used to separate light of the necessary wavelengths. When recording the spectra of the intermediate absorption in the wavelength range 520–700 nm the clink width of the monochromator remained constant.

Recording the kinetics of the optical density changes of the samples was carried out by means of a PEM-77 photoelectron multiplier and a C9-8 digital memory oscilloscope (both from Russia). The kinetics of two-electron reduced benzoviologen form decay were monitored by the change in the optical density at $\lambda = 604$ nm. The transformation of the oscilloscope signal into the kinetic curves was made using the equation

$$\frac{D^{604}(t)}{D^{604}(0)} = \frac{\log[1 - U(0)/U_0]}{\log[1 - U(t)/U_0]}$$

where $D^{604}(0)$ is the optical density of the sample at the initial moment, $D^{604}(t)$ is the current optical density of the sample, U_0 is the background voltage on the photoelectron multiplier, $U(0)$ is the voltage on the photoelectron multiplier at the initial moment and $U(t)$ is the current voltage on the photoelectron multiplier.

The measurements were carried out in 10 cm quartz cell at a temperature of 20 °C. Before the measurements with $[CoEDTA]^-$ as an external (as regards the vesicular cavity) electron acceptor, the dissolved oxygen was removed from the sample by passing Ar over its surface for 1.5 h under continuous stirring.

3. Results

3.1. Formation of CdS nanoparticles in the cavities of lipid vesicles

Consecutive addition of 1 ml of buffer solution (pH 8.2) and 50 μl of 0.5 M solution of Na_2S to 1 ml of the obtained vesicle suspension results in the formation of cadmium sulfide nanoparticles in the inner cavities of lipid vesicles according to the reaction [2]

$$[CdEDTA]_{in}^{2-} + Na_2S \longrightarrow CdS_{in} + H_2EDTA^{2-}$$

where the subscript in indicates the location of a substance in the vesicular cavity. The process of CdS nanoparticles formation was monitored by a change in the UV–visible absorption spectra in the wavelength range 260–540 nm, which is characteristic for CdS absorption.

The CdS nanoparticles, prepared in such a manner inside the vesicular cavity, are known to be able to serve as photosensitizers (photocatalysts) of the electron transfer processes across the lipid membrane [1,2]. To create a system capable of such electron transfer, the lipid membrane is usually "modified" with a mobile primary electron acceptor (electron relay). The change in the optical absorption spectra of the sample containing DML vesicles with growing CdS nanoparticles in the inner cavities and the benzoviologen-modified membrane is shown in Fig. 2. Such samples were found to be more stable and less turbid than those with cetylviologen as the electron carrier. The schematic diagrams of these photocatalytic systems for transmembrane electron transfer are shown in Fig. 3(a).

3.2. 1,4-bis(1,2,6-triphenyl-4-pyridyl)benzene (benzoviologen) as an electron carrier

We used benzoviologen as the electron relay. This highly lipophilic compound seems to be a more promising reversible molecular electron carrier in comparison with lipophilic compounds of a family of simple viologens, e.g. cetylviologen. The structural formula of benzoviologen and its one- and

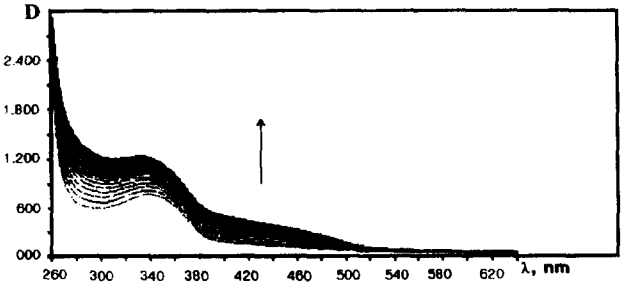

Fig. 2. Changes in the absorption spectra of the suspension of DML vesicles with the benzoviologen-modified membrane (benzoviologen:lipid, 1:100), containing initially 0.3 M K_2[CdEDTA] in the cavities and borate buffer with pH 8.2 in the outer solution upon the addition of 0.5 M Na_2S at a temperature of 20 °C; the spectra are recorded at 150 s intervals. D is the optical density of the sample with 1 cm optical length.

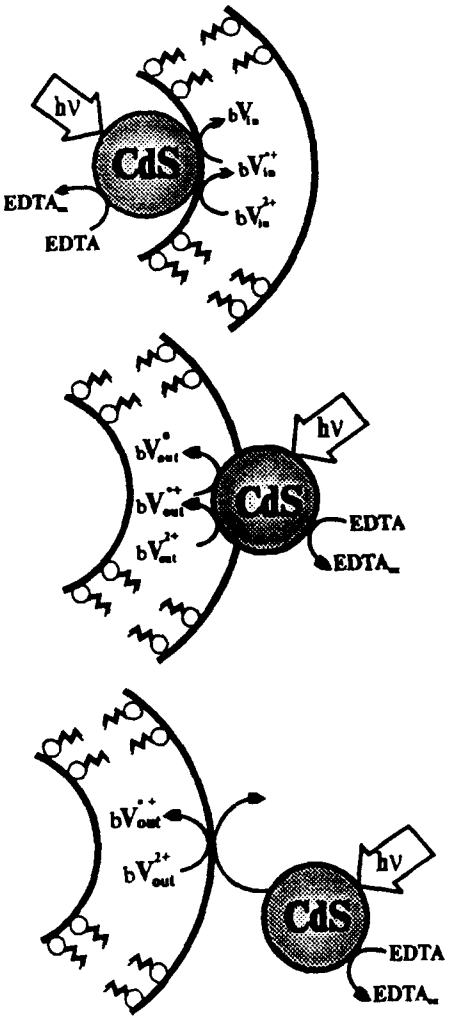

Fig. 3. Schematic views of the designed photocatalytic systems for the interface electron transfer. The subscripts in and out correspond to the inner and outer (with respect to the vesicular cavity) monolayers of the bilayer membrane. $EDTA_{ox}$ are the products of EDTA oxidation (the charge of EDTA anions is omitted). Electron transfer is sensitized by (a) CdS in the inner cavities, (b) CdS, attached on the outer surface of the vesicle membrane, and (c) preliminarily prepared colloidal CdS particles, stabilized by PAA.

two-electron reduced forms are shown in Fig. 1. Both the reduced forms of benzoviologen are stable and easily recorded using visible spectrometry [6].

One can suppose that interaction between positively charged nitrogen atoms of benzoviologen and surface-active anions will be impeded because of their space inaccessibility, thus preventing formation of residues and destruction of the vesicles. Also, the reduced forms of benzoviologen are stronger reductants than those of cetylviologen (e.g. $E^0_{bV^{2+}/bV^{\bullet+}} = -0.48$ V with respect to a normal hydrogen electrode (NHE) [6] against $E^0_{CV^{2+}/CV^{+}} \approx -0.2$ V (NHE) when cetylviologen cations are embedded into the lipid membrane [4]). At the same time, the benzoviologen molecule possesses a conjugated system of double bonds, which seems to allow it to function as molecular "wire" when carrying out the transmembrane electron transfer, thus facilitating this process.

3.2.1. Electron transfer across the border "vesicular cavity–membrane"

The samples for photochemical measurements were prepared in the following way: before sonification, dry lecithin was dissolved in the acetonitrile solution of benzoviologen with the subsequent removal of the solute by evaporation in vacuo under heating at approximately 50 °C. The further procedures were as described in Section 2. When carrying out the photoelectron transfer, the Na_2H_2EDTA and S^{2-} present in the system can serve as electron donors and react with the holes photogenerated in CdS. However, preliminary experiments have shown that the amount of S^{2-} added to the system as well as of H_2EDTA^{2-} released as a result of the formation of CdS nanoparticles are not sufficient to carry out the photoelectron transfer with a noticeable quantum yield. For this reason, upon the preparation of CdS nanoparticles together with the Cd complex an extra amount of an electron donor should be placed into the vesicle cavity. In our experiments, Na_2H_2EDTA with a concentration of 10^{-2} M was added. The synthesized systems for the photoelectron transfer with the membrane-embedded benzoviologen molecules as the electron carrier are schematically shown in Fig. 3(a).

Stationary photolysis experiments were carried out to determine the qualitative features of the photoaccumulation of the reduced forms of benzoviologen and of the quantum yields of this process. The deoxygenated samples were irradiated with a continuous laser light source ($\lambda = 458$ nm) with the light intensity of 0.02 W controlled with the LM2 bolometer. The kinetics of accumulation of both one- and two-electron reduced forms of benzoviologen, the so-called "red" and "blue" forms ($bV^{\bullet+}$ and bV respectively) [6],

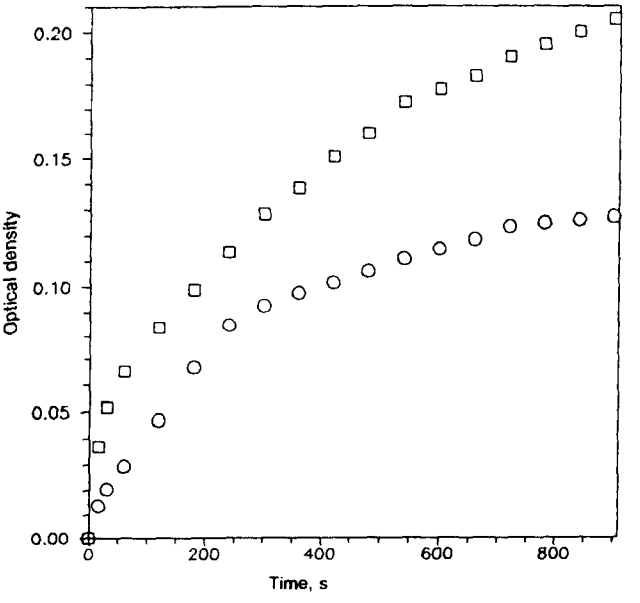

Fig. 4. Dependence of the change in the sample optical density upon the time of its irradiation by continuous laser source ($\lambda = 458$ nm) at two recording wavelengths λ (sample: CdS and Na_2H_2EDTA (10^{-2} M) inside the vesicular cavities; molar fraction of benzoviologen in the DML membrane, 0.01; pH of the outer solution, 8.2): □, $\lambda = 604$ nm; ○, $\lambda = 525$ nm.

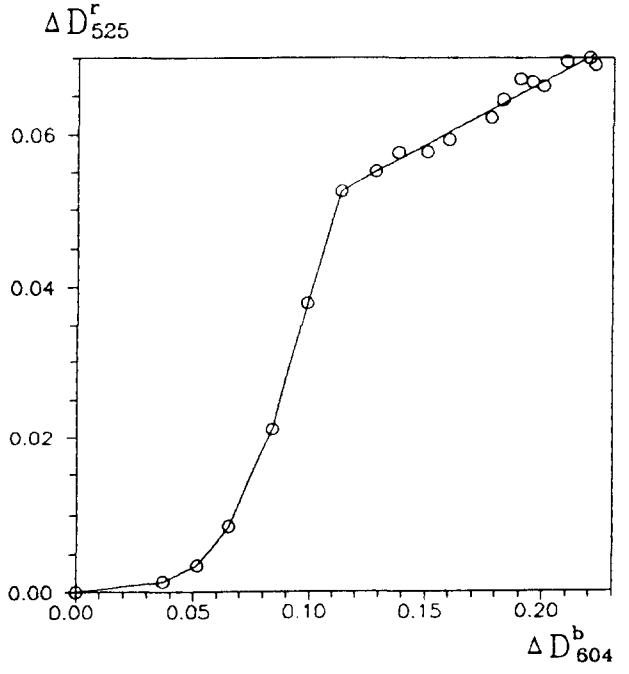

Fig. 5. Correlation of changes in the optical density D at $\lambda = 525$ nm and $\lambda = 604$ nm provided by the accumulation of benzoviologen "red" and "blue" forms respectively under the stationary photolysis of benzoviologen for the EDTA–CdS–bV^{2+} system shown in Fig. 3(a) (molar fraction of benzoviologen in the DML membrane, 0.01; concentration of Na_2H_2EDTA, 10^{-2} M; pH of the outer solution, 8.2).

were monitored by the change in optical density at the absorption maxima wavelengths $\lambda = 525$ nm and $\lambda = 604$ nm correspondingly. An example of the kinetic curves obtained is shown in Fig. 4. It can be easily observed that simultaneous accumulation of the "red" and "blue" forms of benzoviologen occurs rather than a consecutive transition of the "red" form into the "blue" form.

The values of the initial quantum yields of accumulation of the benzoviologen reduced form in the membrane were calculated as described in Section 2 and they were found to be $\phi^{b} = 1.6\%$ and $\phi^{r} = 0.1\%$.

Earlier it was found [6] that, in analogous systems with trisbipyridylruthenium(II) diperchlorate as the photosensitizer of the photoelectron transfer, the initial reduced form of benzoviologen was the "red" form and that in the process of irradiation it gradually transformed into the "blue" form. This has been vividly illustrated by the $\Delta D_{525}{}^{r}$ vs. ΔD_{604} dependence obtained in [6]. A similar $\Delta D_{525}{}^{r}$ vs. ΔD_{604} dependence obtained by us (Fig. 5) drastically differs from that in [6] and shows that at the initial time not only formation of the "red" form but also even more rapid formation of the "blue" form occurs.

3.2.2. Systems with the inverted topology

Upon the addition of 1 ml of the preliminarily prepared 10^{-2} M CdS colloidal solution (particles of 50 Å diameter) to 1 ml of the solution, containing the suspension of vesicles with KCl in the inner cavities, Na_2H_2EDTA in the outer phase and benzoviologen in the membrane, a system of inverted topology, as shown in Fig. 3(c), was obtained.

Irradiation of this sample with a continuous laser source ($\lambda = 458$ nm) after degassing results in the accumulation of "blue" and "red" forms in the membrane as well. The corresponding quantum yields were found to be equal to 0.11% and 0.09% respectively. It should be noted that the value of the quantum yield for the "blue" form is an order less than for the above systems with in-situ synthesized CdS. Thus a formation of primarily "red" form occurs.

We have also made an attempt to synthesize systems of inverted topology with "attached" CdS nanoparticles, as shown in Fig. 3(b). By means of gradual addition of a dilute cadmium chloride solution to the vesicle suspension, containing KCl in the inner cavities, benzoviologen in the membrane and Na_2S with borate buffer in the outer solution, CdS particles adsorbed on the outer surface of the vesicle membrane were obtained. This is confirmed by the optical absorption spectrum of the vesicle fraction after gel filtration, which shows the presence of the adsorbed CdS particles. Upon irradiation of the deoxygenated sample by the light with $\lambda = 458$ nm, we observed mainly the formation of the benzoviologen "blue" form as it occurs for the above systems with the "normal" topology (Fig. 3(a)).

The results obtained allow us to conclude that in the case of the unadsorbed CdS particles (Fig. 3(c)) a collision of an excited CdS nanoparticle and benzoviologen molecule results in the transfer of one electron and the formation of the "red" form, while in the case of the adsorbed CdS particles (Figs. 3(a) and 3(b)) predominantly the "blue" form is created initially. Also this allows us to conclude that in-situ synthesized CdS nanoparticles inside the vesicular cavities are probably also adsorbed on the inner membrane surface.

3.2.3. Identification of the primary reduced form of benzoviologen

To identify the form of reduced benzoviologen originating from the primary photochemical process, we used the method of pulse photolysis. The experiment was carried out by detecting a transient absorption of intermediate compounds in the wavelength range 520–700 nm at different time moments after the light flash. The obtained absorption spectrum is shown in Fig. 6. It is seen clearly that primarily the "red" form is formed and only a small amount of the "blue" form. This observation confirms that the primary elementary photochemical process in the system on the basis of CdS nanoparticles is a photoinduced transfer of one electron from this CdS nanoparticle to the molecular acceptor.

The results obtained allow us to conclude that the reduction of the electron carrier benzoviologen onto one and two electrons occurs step by step as was shown in [6]. However, the predominant formation of the two-electron reduced form of benzoviologen on continuous illumination in the situation with the "membrane-attached" (both inside or outside) CdS nanoparticles shows much faster photoreduction by the second electron than by the first electron. This can result firstly

from a small mobility of the benzoviologen molecule in the lipid membrane, which restricts removal of the one-electron reduced form of benzoviologen from the attached geminating CdS nanoparticle, and secondly from the large space accessibility of the photosensitizer. In fact, in trisbipyridylruthenium(II) systems [6] where the mobile photosensitizer is dissolved in the water phase of the vesicular cavity, the electron transfer across the interface border "vesicular cavity–membrane" occurs most probably upon a collision between the excited photosensitizer molecule and the electron carrier. In the case of our systems of the type shown in Fig. 3(a), the CdS nanoparticle is adsorbed on the inner surface of the membrane and therefore provides a greater contact surface area with the electron carrier. One can suggest that at steady illumination the primary process of two-electron reduced form formation occurs mostly in the sites of the inner monolayer of the lipid membrane, where there is direct contact of benzoviologen molecule with adsorbed CdS.

The method of pulse photolysis was also used to investigate the kinetics of the benzoviologen "blue" form decay with $[CoEDTA]^-$ as an electron acceptor in one case and O_2 in the other. The concentration of $[CoEDTA]^-$ in the outer solution was equal to 10^{-3} M. Anions of $[CoEDTA]^-$ cannot diffuse across the lipid membrane; that is why the interaction occurs only with the benzoviologen reduced forms located in the outer monolayer of the vesicle membrane. The obtained dependences of the "blue" form concentration vs. time (Fig. 7) are well approximated by a straight line. This allows us to suggest the existence of first-order kinetics upon the interaction between the "blue" form and an electron acceptor. The corresponding rate constants, determined from the slope of the kinetic curves, were found to be equal to 6 s^{-1} for $[CoEDTA]^-$ as the acceptor and 36 s^{-1} for the oxygen-saturated system. Note that the highest rate of interaction with O_2 is easily understandable owing to high solubility of O_2 molecules in the lipids. It should be mentioned also that in the case of $[CoEDTA]^-$ we actually observed the transmembrane electron transfer, i.e. transfer across two interface borders "vesicular cavity–membrane" and "membrane–outer solution" (Fig. 8).

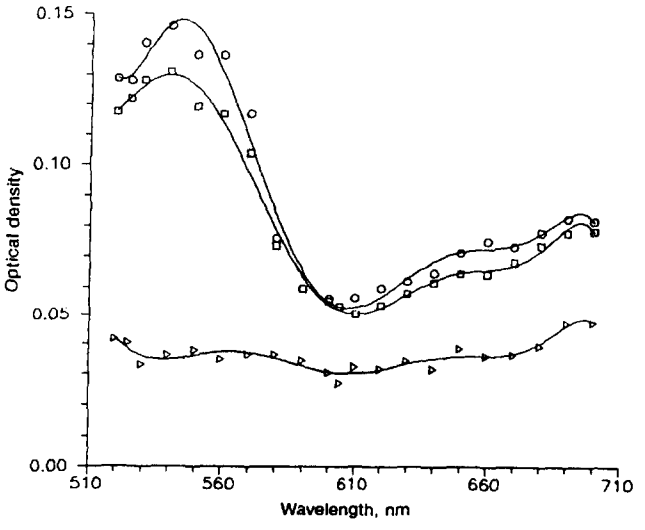

Fig. 6. Spectra of an intermediate absorption of the sample provided by pulse photolysis of the Na_2EDTA–CdS–bV^{2+} system and recorded at different time periods after the flash (sample, CdS and Na_2H_2EDTA (10^{-2} M) inside the vesicular cavities; molar fraction of benzoviologen in the membrane, 0.01; pH of the outer solution, 8.2): ○, 78 μs; □, 108 μs; △, 1200 μs.

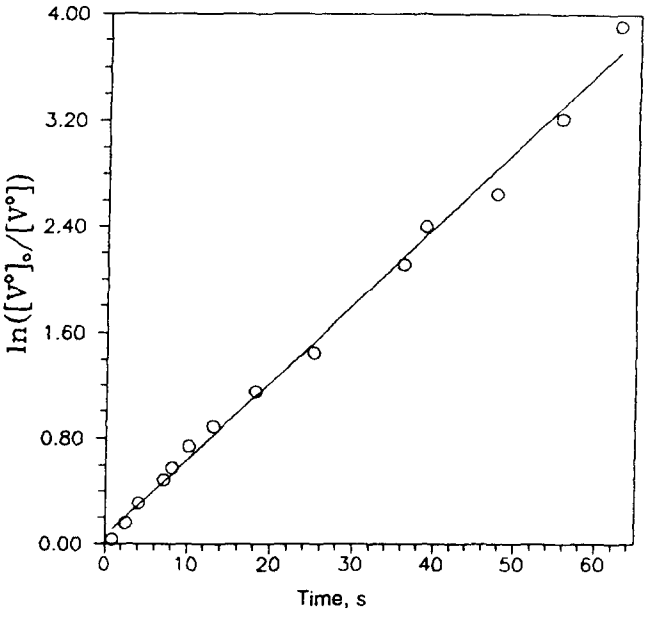

Fig. 7. Dependence of two-electron reduced benzoviologen form ("blue") (V^0) concentration on time, provided by pulse photolysis, where $[V^0]_0$ is the "blue" form concentration at the initial time moment after the flash for the system shown in Fig. 8 (sample, CdS and Na_2H_2EDTA (10^{-2} M) inside the vesicular cavities; molar fraction of benzoviologen in the DML membrane, 0.01; pH of the outer solution, 8.2; concentration of $[CoEDTA]^-$ in the outer solution, 10^{-3} M).

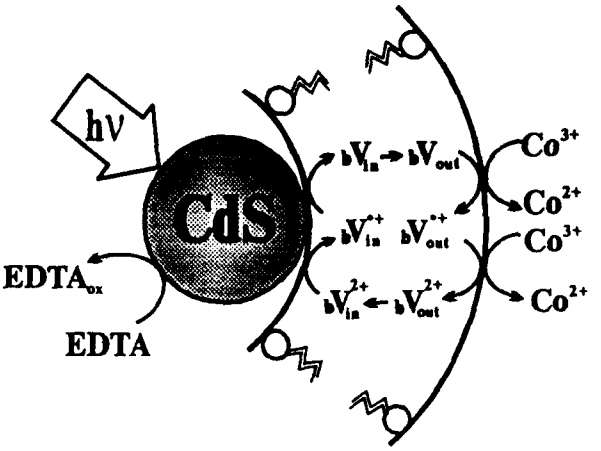

Fig. 8. Schematic view of the designed photocatalytic system for the transmembrane electron transfer. Co^{3+} and Co^{2+} stand for $[CoEDTA]^-$ and $[CoEDTA]^{2-}$ respectively.

4. Discussion and conclusions

The above results confirm the possibility of synthesizing rather stable and photoactive systems for vectorial transmem-

brane electron transfer on the basis of semiconductor nanoparticles and a novel lipophilic electron relay benzoviologen. The main peculiarity of the latter electron relay is the existence of its two easily detectable reduced forms, each of them possessing a strong reducing ability. The above preliminary non-direct estimation of the transmembrane mobility of such reduced forms (from the data on reactivity with $[Co\text{-}EDTA]^-$) gives a value not less than $10\ s^{-1}$, which is indeed comparable with the respective mobility (or even greater) of simpler lipophilic viologen-like species [7,8].

Proceeding from the above reasoning, one can suggest the following mechanisms for the transmembrane electron transfer under consideration:

$$CdS + bV_{in}^{2+} \overset{h\nu}{\longleftrightarrow} CdS^+ + bV_{in}^{\bullet+} \quad (1)$$

$$CdS + bV_{in}^{\bullet+} \overset{h\nu}{\longleftrightarrow} CdS^+ + bV_{in} \quad (2)$$

$$EDTA^{4-} + CdS^+ \longrightarrow CdS + EDTA_{ox}^{4-} \quad (3)$$

$$bV_{in} + bV_{out}^{2+} \longrightarrow bV_{in}^{\bullet+} + bV_{out}^{\bullet+} \quad (4)$$

$$bV_{in} \longleftrightarrow bV_{out} \quad (5)$$

$$bV_{in}^{\bullet+} \longleftrightarrow bV_{out}^{\bullet+} \quad (6)$$

$$bV_{out} + Ox \longrightarrow bV_{out}^{\bullet+} + Ox^- \quad (7)$$

$$bV_{out}^{\bullet+} + Ox \longrightarrow bV_{out}^{2+} + Ox^- \quad (8)$$

where the subscript out corresponds to the outer monolayer of the bilayer lipid membrane (see Fig. 8). $EDTA_{ox}^{4-}$ represents the irreversibly oxidized forms of $EDTA^{4-}$ anions. Reactions (7) and (8) are displayed for the case when there is an oxidant (Ox) (the secondary-electron acceptor) in the outer as regards the vesicular cavity phase. To draw a certain conclusion about the roles of different reactions, a more comprehensive experimental study of the system is necessary.

A principal point in the mechanism of the transmembrane vectorial charge transfer with the use of benzoviologen is the role of each of its reduced forms. There is no doubt that the non-charged two-electron reduced "blue" form bV of benzoviologen should possess the highest transmembrane mobility, thus determining most of the dynamic transmembrane phenomena as was recently determined for more lipophilic viologens too [8]. An important role here belongs to the process of disproportionation of various redox forms of viologens.

Unexpectedly, under steady illumination of the system with the "membrane-attached" CdS nanoparticles, a predominant accumulation of the "blue" form was observed rather than of the one-electron reduced "red" form, despite the fact that the primary photochemical act is indeed only one-electron reduction of the benzoviologen moiety. Comparison of this observation with the respective behavior of a similar benzoviologen-containing system differing mostly in the more mobile nature of the photosensitizer allows us to conclude that the predominant formation of the "blue" form in our case is not a sequence of an efficient disproportionation or dismutation of various forms of benzoviologen. Vice versa, most probably the observed photochemical peculiarity of the CdS–benzoviologen system could originate from the specificity of the construction of the "hybrid" semiconductor nanoparticles–molecular electron relay systems stabilized by lipid bilayers. Indeed, according to various estimations [2,3], the typical linear size of the semiconductor nanoparticle aggregates formed in situ inside the vesicular cavities is on the scale of 30 Å or even more, if the nanoparticles appear to be non-spherical and spread alongside the surface of the lipid membrane. Taking into account the small size of the vesicles themselves (in the case of DML vesicles the internal and external diameters are equal to about 100 Å and 200 Å respectively [7]) and a restricted lateral mobility of the electron relay, one should expect that in conditions of rather intensive illumination the primarily formed moieties of the "red" form cannot escape contact with the (most probably) geminate CdS nanoparticles before the next excitation of the CdS nanoparticle. This can lead to the predominant repetitive reduction of the one-electron reduced form of benzoviologen. Note also that, at the lipid:benzoviologen molecular ratio of 100:1, each vesicle contains on average 30–40 molecules of benzoviologen.

It is of great interest to mention also the much higher apparent values of the quantum yield of the formation of two-electron reduced "blue" form than that of the "red" form (compare $\phi^b = 1.6\%$ and $\phi^r = 0.1\%$). It is evident that, owing to a two-step photochemical process of formation of the "blue" form, the apparent quantum yield of this process should be a combination of the real quantum yields of the first and second steps, the resulting value being no greater than the minimum value of these elementary quantum yields. Thus one can expect that these elementary quantum yields are in fact much higher (perhaps by an order of magnitude) than the measured value of 1.6%. This demonstrates the really high efficiency of the elementary redox photochemical processes on the "attached CdS–lipid membrane with the benzoviologen inclusion" boundary interface and the good prospects for further improvement of the quantum efficiency of the system under discussion. Simultaneously, the data on the apparent quantum yields show that the observed photochemical formation of the one-electron reduced "red" form at the steady illumination results from a "by-process" rather than from a photochemical reduction of the benzoviologen molecules located in the immediate vicinity of the attached CdS nanoparticle.

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